

THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

THE STRUCTURE AND PHASE TRANSFORMATIONS IN Al-Li-Mg ALLOYS CONTAINING Zr AND Sc.

I M Khatsinskaya¹, O E Grushko¹, L M Sheveleva¹, N I Kolobnev¹, P.D.Couch² and W.S.Miller².

1. VIAM, 17 Radio Street, 107005, MOSCOW, Russia
2. Corporate Research Laboratory, Hoogovens Groep BV, Postbus 10,000, 1970 CA IJmuiden, Netherlands.

Abstract

The study of the phase transformations occurring in Aluminium-lithium-magnesium alloys with scandium and zirconium additions has been carried out. The techniques used in the analysis included optical microscopy and differential scanning calorimetry (D.S.C.). The structures and precipitates developed during solidification have been identified. Zirconium additions are shown to be more effective than scandium additions for controlling the cast structure of the alloy. Two eutectic phases have been shown to form in the cast ingots, these phases are δ (AlLi) and S_1 (Al₂MgLi). The magnesium-lithium content of the alloy has been shown to control which eutectic forms. Comparison of the D.S.C. results is made with existing literature and is in close agreement. The precipitation sequences observed in the alloys are reported.

Introduction

Since 1970, the 1420 (Al-5.0%Mg-2.0%Li-0.4%Mn), developed at VIAM, has been used as the main structural material in riveted structures of Russian aircraft. This allowed the structural weight of aircraft to be reduced by 10-12% ^(1,2). The use of this alloy has also enabled a reduction of weight by 24% in replacing a riveted 2024 structure with a welded tank. However, the alloy has a number of drawbacks in particular its rather low 0.2%PS which limits its use in higher strength aerospace structures. Hence several alloy modifications with improved technological efficiency, high strength characteristics and corrosion resistance were developed ^(3,4,5). These include changes in the dispersoid forming addition from Mn to Zr and/or Sc, and changing the amounts of Mg and Li.

The objective of this study is to examine the alloys of Al-Li-Mg system with Zr and Sc additions using an experimentally designed programme. The programme provides a comprehensive study of the alloy system including processing, microstructure and mechanical properties⁽⁶⁾. In this paper the effect of alloy chemistry on the cast microstructure is discussed.

Experimental

Al-Li-Mg alloys with zirconium/scandium additions, see table 1 ⁽⁶⁾ for all alloy chemistries evaluated, have been prepared in standard electric resistance furnaces, with the weight of each melt approximately 10kg. The zirconium/scandium additions were introduced to the melt as master alloys and successful dissolution was achieved at a melt temperature of 760°C. LiCl-KCl flux was added to the surface of the melt prior to lithium addition to reduce lithium loss and hydrogen pick-up during a hold of 30 minutes at 720°C for complete mixing and degassing. The alloys were then poured into a cast iron water-cooled mould with a diameter of 70 mm producing ingots weighing 2.5kg (i.e. 4 ingots produced from each melt composition).

The melt additions used had the following analyses (wt% unless otherwise stated):

- aluminium (Fe-0.01%, Si-0.006%, Na-6ppm)
- magnesium (total impurity content 0.05%)
- lithium LE1 grade (total impurity content 0.1%)
- aluminium-zirconium master alloy (2 % zirconium)
- aluminium-scandium master alloy (2 % scandium)

The ingots were sectioned for microstructural assessment and the metallographic specimens prepared. The cast grain structures were revealed by anodising in 2% HBF₄ solution with observations made using polarised light. In order to identify the intermetallic compounds present, the metallographic specimens were etched in concentrated H₃PO₄ for 30-40 seconds. Determination of the volume fraction of the constituent particles was made using the linear intercept technique.

Differential scanning calorimetry (D.S.C.) experiments have been conducted on samples 12mm diameter by 6mm in height weighing approximately 1.8g using a Sinku-Riko SH3000M adiabatic scanning calorimeter. The D.S.C. cell was purged continuously during testing with Argon gas and a heating rate of 3°C/min was used.

Results

Table 1 details the actual alloy chemistries chosen to illustrate the effect of chemistry on structure in the present paper. Typical micrographs of as-cast grain structures are presented in figures 1 a-c for alloys 2, 3 and 4 respectively. There is a significant reduction in the grain size with increase in the wt% of zirconium present at the same level of Li-Mg content with the scandium alloy developing much larger grains. Hence the zirconium addition has a grain refining effect during cast structure formation. The average grain sizes from each alloy are presented in table 2 and emphasise the influence of zirconium on the cast structure developed. This effect was typical of all alloys examined.

Typical micrographs for precipitate assessment are presented in figures 2 a-c for alloys 2, 5 and 6 respectively, etching in concentrated H₃PO₄ being necessary to observe the non-equilibrium eutectics which develop along grain boundaries during solidification. Two

different types of precipitates, namely the S_1 (Al_2MgLi) and δ ($AlLi$) phases develop and are dependent on the magnesium and lithium content, see table 2. Alloy 1, low magnesium and low lithium shows only occasional δ precipitation in the as-cast state. Alloy 2 with the low magnesium-lithium content shows only the δ phase precipitate (dark coloured) is developed during solidification, see figure 2a. The high magnesium-low lithium alloy, alloy 5, indicates only the formation of S_1 phase (light grey) as presented in figure 2b. Whilst, the middle chemistry alloy, alloy 6, develops both the light-grey S_1 phase and the black δ phase precipitates during solidification.

Typical D.S.C. traces from alloys 2, 5 and 6 are presented in figures 3 a-c respectively. Using the D.S.C. plots it is possible to distinguish between the precipitate reactions which are observed. Thus alloy 2 shows three reaction peaks at $\approx 110^\circ C$, $\approx 220^\circ C$ and $\approx 430^\circ C$, alloy 5 also produces three reaction peaks at $\approx 110^\circ C$, $\approx 190^\circ C$ and $\approx 410^\circ C$. Alloy 6 produces four reaction peaks at $\approx 110^\circ C$, $\approx 210^\circ C$, $\approx 240^\circ C$ and $\approx 400^\circ C$. Hence as the magnesium content is increased from alloy 2 to alloy 6 the sequence of precipitation reactions remains unchanged but the temperature at which δ' phase is seen to precipitate is offset to lower temperatures. When comparison is made between the high magnesium alloys an increase in the lithium content produces a double reaction peak in the temperature range $150 \rightarrow 300^\circ C$. Hence the microstructure and D.S.C. assessment of the alloys shows a significant influence of magnesium-lithium content on the type of phases which can develop in the alloys under investigation.

Discussion

For a fixed magnesium-lithium content the influence of zirconium on the solidified grain structure is quite dramatic. A transition has been seen from a coarse grain structure in the zirconium free alloy to a very fine grain structure in the alloy containing a 0.12wt % addition of zirconium. There has also been shown a reduction in grain size with increase in the wt % of zirconium addition, i.e. 0.08% Zr produces grain sizes of approximately $50\mu m$ whereas 0.12% Zr produces grain sizes of approximately $35\mu m$. The scandium addition, by itself, however has no effect on the solidified grain structure with very coarse grains produced (approximate size $200\mu m$). It is anticipated that the zirconium and scandium additions react to form aluminides which act as structure modifiers. The zirconium aluminide (Al_3Zr) exists as crystals in the liquid which act as heterogeneous nucleation sites hence a finer grain structure forms with increased zirconium content. A similar mechanism would be expected for the scandium addition with the formation of scandium aluminide (Al_3Sc). From the literature⁽⁷⁾ it is evident that scandium has greater solubility in aluminium than the zirconium, therefore the majority of the scandium is retained in solution during solidification but the zirconium crystallises out as Al_3Zr . Thus, the 0.20 wt% scandium addition is too low to have an influence on grain structure. In the scandium + zirconium alloy, alloy 3, grain refinement is solely due to the presence of zirconium at a slightly reduced level i.e. 0.08wt% and hence larger grains are produced than for the 0.12wt% zirconium alloy.

A significant influence of magnesium-lithium content on ingot precipitate structure has been observed both by optical microscopy and D.S.C. assessment at low Li/Mg content. It has been seen, figure 2a, that at the magnesium content of 3.5% and lithium content 1.9% only

δ phase is observed. An increase in the magnesium content to 5.1% accompanied by a slight decrease in lithium content to 1.72%, figure 2b, single S_1 phase is observed. At the magnesium content of 5.1% but higher lithium level of 2.42% both S_1 and δ phases are formed, figure 2c. From this information it can be assumed that as the magnesium content is increased 3.5% \rightarrow 5.1% for relatively low lithium contents in the range 1.7 - 1.9 % there is a change in the type of eutectic developed in the cast ingot, i.e. δ phase \rightarrow S_1 respectively. Hence at magnesium contents \leq 3.5% there is insufficient magnesium present to form S_1 phase and, δ phase is preferentially formed. It is also true that the dominant reaction in the high magnesium alloy produces the S_1 phase leaving no free lithium available for δ phase formation. However, in the high magnesium - high lithium alloy, alloy 5, both S_1 and δ phase develop because there is excess magnesium and lithium present.

The D.S.C. results, figures 3 a-c, highlight the different precipitation sequences observed in each alloy and the D.S.C. traces are in good agreement with those presented previously ⁽⁸⁾ for Al-Cu-Mg-Li alloys. However, the one notable difference is the precipitation of the S_1 (Al_2MgLi) phase rather than S (Al_2CuMg) due to the different chemistries involved. The S_1 phase being observed in the temperature range of δ' phase formation rather than in combination with δ phase⁽⁸⁾. It has been reported⁽⁸⁾ and observed herein that the reaction peak at $\approx 110^\circ C$ found in all alloys is related to GPB zones and the reaction at $\approx 190^\circ C$ is associated with δ' phase. It is suggested that the higher temperature reaction peak at $\approx 230^\circ C$, alloy 2, is associated with S_1 phase formation (some δ' precipitation is also expected in the lower temperature range of the peak). The results indicate that as the magnesium content is increased (for alloys 1.7 \rightarrow 1.9 wt% Li) the tendency to form δ' precipitate is increased suggesting reduced solubility of lithium. An increase in the lithium content of high magnesium alloys, alloys 5 and 6, produces a double reaction peak in the range 150 \rightarrow 300 $^\circ C$, which suggests that the chemistry is rich enough in alloy 6 to promote significant precipitation of both the phases δ' and S_1 which subsequently appear as separate peaks in the D.S.C. trace. Hence the influence of alloy chemistry on the precipitation sequence in the current alloys has been analysed. These results follow the commercial ageing treatments applied to these alloy types, prolonged hold time at 125 $^\circ C$ to develop δ' precipitates in accordance with the treatment used for alloy 1420 to produce average tensile properties accompanied by high corrosion resistance. Or alternatively ageing at 165 $^\circ C$ to develop peak strength properties forming both δ' and S_1 precipitates. It should also be pointed out that the zirconium/scandium additions were seen to have no influence on the precipitation reactions in the present alloys, but only to influence the morphology of the eutectics developed during solidification at grain boundaries

Conclusions

- (1) Additions of zirconium/scandium to Al-Mg-Li alloys have been made and it has been shown that the zirconium content significantly refines the cast grain structure produced. For the alloy (nominal chemistry Al-3.5Mg-2.25Li) 0.12% Zr develops a grain size $\approx 35\mu m$ whereas 0.20% Sc develops $\approx 200\mu m$ grains. Hence zirconium is a more effective structure modifier than scandium for Al-Mg-Li alloys.
- (2) The alloy chemistry has been shown to control the eutectic microstructure developed

during solidification. The two eutectic precipitates which form are δ (AlLi) and S_1 (Al_2MgLi). It has been shown that the proportion of magnesium-lithium present controls the type of eutectic which forms. High magnesium-low lithium produces S_1 , low magnesium- low lithium produces δ , and high magnesium-high lithium produces both S_1 and δ .

- (3) The D.S.C. results show that the sequence of precipitation reactions in the present alloys are consistent with those reported previously. The double peak in alloy 5 for the high magnesium-high lithium alloy highlighting the individual temperatures for the δ' reaction and the S_1 reaction.
- (4) There was no influence of zirconium/scandium addition on the precipitation sequence in the present alloys.

References

1. I.N. Fridlyander, V.F. Shamray and N.V. Shiraeva "Metally" 1965 N2 p153-158.
2. I.N. Fridlyander, A.G. Bratukhin and A.G. Davidov in 6th Aluminium-lithium conference 1991 V1 p35-42.
3. V.G. Kovaliov, O.E. Grushko, O.E. Sheveliova et al Russian Patent AC USSR N1566759 22-Jan-1990
4. N.I. Turkina and E.V. Semenova Light Alloys Technology 1991 N1 p57-59.
5. I.N. Fridlyander, N.I. Kolobnev and O.E. Grushko et al. Russian Patent AC USSR N1367517 16-Jan-1986.
6. This Conference.
7. L.F. Mondolfo, Aluminium Alloys: Structure and Properties (London: Butterworths 1979), p366, p413.
8. A. Luo, D.J. Lloyd, A. Gupta and W.V. Youdelis, Acta Metallurgica et Materialia, Vol.41, (1993), p769.

Table 1. The alloy chemistries under investigation.

Alloy No.	Mg (wt%)	Li (wt%)	Sc (wt%)	Zr (wt%)	Al.	Mg/Li
1	2.0	1.6	0.23	0.00	bal.	1.25
2	3.5	1.90	0.20	0.00	bal.	2.05
3	3.5	2.30	0.12	0.08	bal.	1.52
4	3.5	2.25	0.00	0.12	bal.	1.55
5	5.1	1.72	0.23	0.00	bal.	2.97
6	5.1	2.42	0.11	0.08	bal.	2.11

Table 2. The average grain sizes and the eutectic precipitates developed during solidification of the ingots.

Alloy No.	Average Grain Diameter (μm)	Precipitate Type
1	425	occasional δ (AlLi)
2	200	δ (AlLi)
3	50	δ (AlLi), S_1 (Al_2MgLi)
4	35	δ (AlLi), S_1 (Al_2MgLi)
5	250	S_1 (Al_2MgLi)
6	22	δ (AlLi), S_1 (Al_2MgLi)

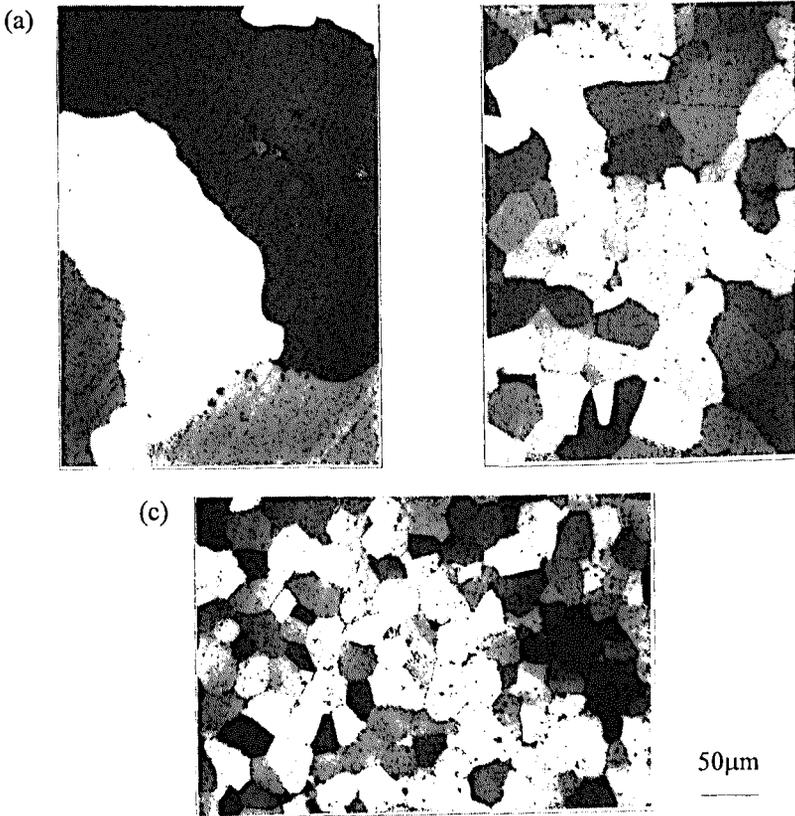


Figure 1. Typical grain structures produced in (a) Alloy 2, (b) Alloy 3 and (c) Alloy 4.

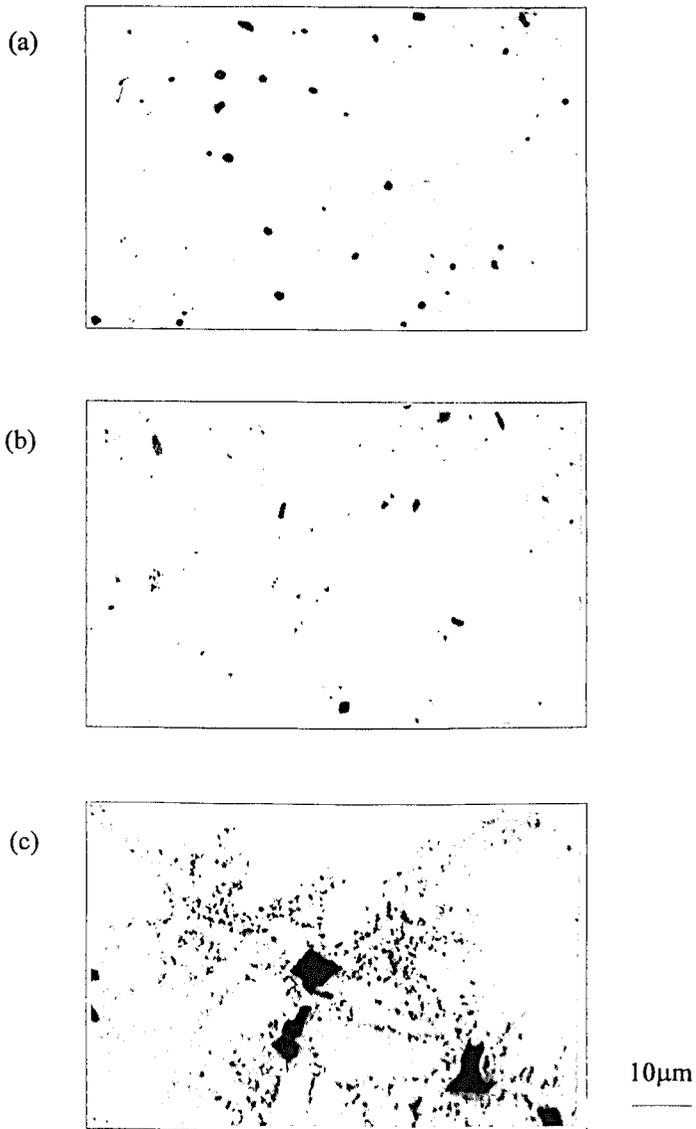


Figure 2. Typical micrographs taken from (a) Alloy 2, (b) Alloy 5 and (c) Alloy 6, showing the eutectic precipitates formed during solidification.

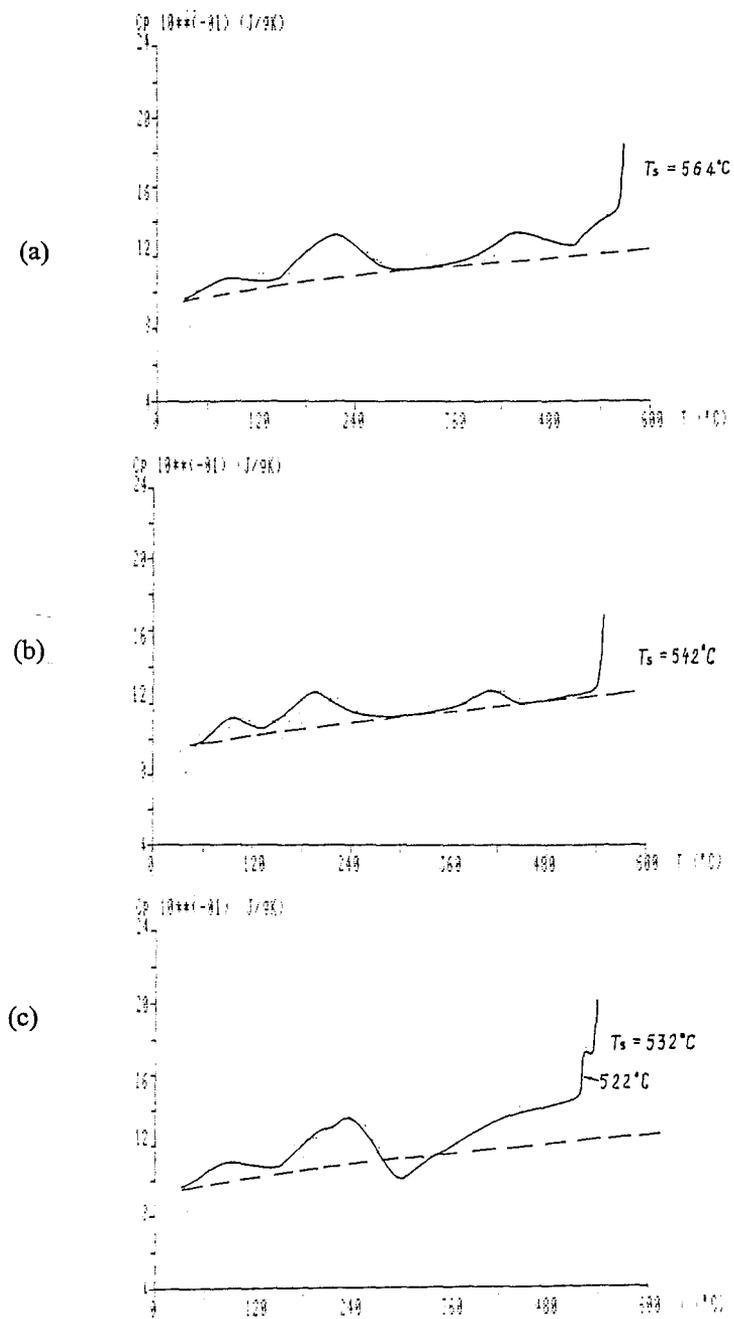


Figure 3. Typical D.S.C. traces produced from (a) Alloy 2, (b) Alloy 5 and (c) Alloy 6.